INFLUENCE OF PRE-OZONATION AND MEDIA TYPE ON BIOLOGICAL ACTIVATED CARBON (BAC) PERFORMANCE

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Activated Carbon has long been used as a potable water filtration media for the removal of Dissolved Organic Carbon (DOC) that would otherwise lead to chlorine decay, regrowth in distribution networks and elevated THM levels.

Australia and New Zealand have widely adopted Biological Granular Activated Carbon (BAC) filtration for the selective removal of that fraction of the DOC that most contributes to chlorine decay - Bio-Degradable Dissolved Organic Carbon (BDOC).

In the BAC process, DOC is converted to biomass by naturally occurring biology that colonise the surface of GAC, excess biomass being eliminated during backwash. This strategy for GAC use avoids requirement for regeneration or replacement, typical bed life is 15 years.

Ozonation is a complimentary step to BAC filtration by converting some of the DOC into BDOC thus greatly enhancing total DOC reduction.

Previous studies show that during cooler water periods, biological activity of BAC filters decreases. This, if not effectively managed, can lead to breakthrough of DOC and BDOC in the BAC filtered water.

This pilot plant study looks at the effect of activated carbon type on BAC performance, by comparing two different steam activated, coal based carbons (the most common type of BAC in Australia and New Zealand) during winter months.

Previous studies show that the presence of ozone prior to the BAC filters significantly influences the character of the carbon both biologically and physically. This study followed previous work and looked at the influence of pre-ozonation on the BAC filtered water quality, in particular the ability of the carbon filters to reduce DOC and manganese both in the presence and absence of ozone.

Biological diversity of the BAC pilot columns was examined (through DNA profiling and SEM) to determine the impact of different activated carbon media, the presence and absence of ozonation, and water temperature.

KEYWORDS

Biological Activated Carbon, Ozonation, Biological Diversity, Organics Removal, Manganese

PRESENTER PROFILE

After graduating with a Bachelor of Science (Chemistry), Peta has worked in the water industry for over 20 years. She runs a consulting and applications research laboratory business in Melbourne, Australia specialising in ozone and activated carbon treatment processes. Research Laboratory Services conducts BAC aging profiles, BDOC and AOC analysis for most of the full scale BAC plants in Australia and NZ. In addition to the fully equipped water and carbon testing laboratory in Melbourne, RLS can also supply skid mounted pilot plant hire, experimental design, project management and operational staff for pilot plants for ozone or activated carbon projects.

1 INTRODUCTION/ BACKGROUND

The annual BAC Aging Profile Analyses for Kyneton WTP (operated by Veolia in the cool climate region of Victoria) in May 2014 showed that there were significantly higher concentrations of manganese present in the acid soluble ash content of the media, particularly at greater depths (increase of 466% from July 2013 data at 2 metre depth). It was thought the redistribution of the manganese throughout the filter media could be attributed to an ozone generator shut down for approximately 8 days prior to sampling the media, thereby supplying the BAC filters with non-ozonated feed water.

Investigation into why the manganese had concentrated in the media required further biological analysis of the media, including SEM to assess if the manganese was assimilated within/by the biology or whether it had been adsorbed onto the carbon. This investigation showed that the media samples from May 2014, collected after the ozone system outage, had elevated levels of biology across the entire bed depth, coupled with highly distributed manganese concentrations. SEM analysis identified significant build-up of iron and manganese oxidising bacteria at all depths sampled, as well as evidence of the presence of protozoa in the BAC surface filter media.

The September 2014 samples, taken four months after ozone reinstatement, display an overall reduction of manganese on the carbon. Microbial colony counts were reduced at 1 metre and 2 metre depths. SEM images for the September samples also indicated changes to the mineralogy and biodiversity of the carbon. In spite of the increased biology (including evidence of higher life forms such as protozoa and less visible heterotrophic bacterium) and elevated manganese levels in the media in May 2014, water quality analysis indicates that the Kyneton BACs had similar organics removal from the water in both May and September.

Following on from these studies of the full scale Kyneton BAC Filters, four BAC pilot plant columns were commissioned at the nearby Castlemaine WTP (operated by Veolia) from June- September 2015. Two columns were filled with established Castlemaine BAC filter media containing viable biofilm. The other two were filled with BAC filter media which had been sterilized by heating at 105^{o}C for 24 hours and then triple rinsed to remove dead biofilm. These columns were fed with ozonated water from the full scale plant and were set-up with an EBCT of 30 minutes. This pilot plant study showed that effluent from the sterilised columns contained higher concentrations of manganese and organics (UV254, colour and DOC) than the feed water suggesting that destruction of the biology was highly detrimental to filter performance and BAC effluent quality. This study showed that it took approximately 20 days for the manganese to stop leaching from the sterilised columns and 50 days for the DOC reduction of the sterilised columns to match that of the non-sterilised carbon. Please note that this pilot plant was run over the cooler water temperature months.

After verifying the importance of biology on the BAC media a new pilot project using two different virgin carbons – Acticarb GA1000N and GS1300 - was undertaken on-site at Castlemaine WTP. The results of this project are described within this paper.

2 METHODOLOGY/ PROCESS

Five pilot plant columns were set-up onsite at the Castlemaine Water Treatment Plant (CWTP), operated by Veolia under a 25 year BOOT contract with Coliban Water. Columns 1-4 were fed with ozonated water from the full scale plant and Column 5 was fed with CMF water (non-ozonated). The media in each of the columns is shown below:

- Column 1 – Established BAC media from the onsite filters
- Column 2 – Acticarb GA1000N 8x30 mesh - steam activated, coal based activated carbon
- Columns 3-5 – Acticarb GS1000N 8x30 mesh - steam activated, coal based activated carbon

All columns operated at an average EBCT of 12 minutes, were backwashed once a week and operated for 12 months. Water samples were initially collected weekly to determine the influence of the virgin carbon's adsorptive capacity, and then monthly samples were collected for the following analyses:

- pH, DO, turbidity
- Organics – DOC, BDOC, UV254, Colour
- Minerals – Total and soluble aluminium, iron, manganese and calcium
- Biological – plate counts, ATP
- Nutrients and media analysis (plate counts, ATP, and DNA profiling) were conducted seasonally

3 RESULTS/ OUTCOMES

3.1 FEED WATER QUALITY THROUGHOUT THE TRIAL

Table 1 summarises the feed water quality for the pilot columns throughout the trial.

Parameter	n	Ozonated Feed (Columns 1-4)			CMF Feed (Column 5)		
		Mean	*Min*	*Max*	*Mean*	*Min*	*Max*
Temp (^{o}C)	34	16.8	8.9	21.8	16.8	8.9	21.8
Ozone Residual (mg/L)	34	0.33	0.17	0.48	NA	NA	NA
pH	19	7.0	6.7	7.1	6.9	6.7	7.1
Dissolved Oxygen (ppm)	16	9.6	8.9	11.6	8.5	7.1	10.4
Turbidity (NTU)	19	0.2	0.1	0.5	0.2	0.1	0.2
Colour (CPU)	19	1.1	0.1	1.6	2.6	0.5	4.8
UV254 (Abs/cm)	19	0.046	0.063	0.033	0.078	0.047	0.099
DOC (mg/L)	19	4.2	3.2	4.9	4.3	3.1	5.0
BDOC (mg/L)	16	1.1	0.5	1.7	0.7	<0.1	1.6
Total Aluminium (mg/L)	17	0.11	<0.1	0.25	0.11	<0.1	0.26
Soluble Aluminium (mg/L)	17	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total Iron (mg/L)	17	0.005	<0.001	0.012	0.005	<0.001	0.023
Soluble Iron (mg/L)	17	<0.001	<0.001	0.003	<0.001	<0.001	0.006
Total Manganese (mg/L)	17	0.007	0.001	0.051	0.005	<0.001	0.043
Soluble Manganese (mg/L)	17	0.007	<0.001	0.049	0.005	<0.001	0.041
Total Calcium (mg/L)	17	7.5	6.7	8.8	7.5	6.6	8.7
Total Ammonia (mg/L)	2	0.02	<0.01	0.03	0.03	<0.01	0.05
Total Nitrogen (mg/L)	2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total Phosphorus (mg/L)	2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 1: Feed Water Quality

3.2 ORGANICS REDUCTION

Initially the virgin carbons showed strong DOC reduction (Figure 1) with Acticarb GS1000N in the presence of ozonated feed water (Columns 3 and 4) achieving maximum percent reductions of 95 and 94% respectively. The other columns also showed high maximum percent reductions within the first few weeks of operation (Column 2 = 82%; Column 5 = 87%).

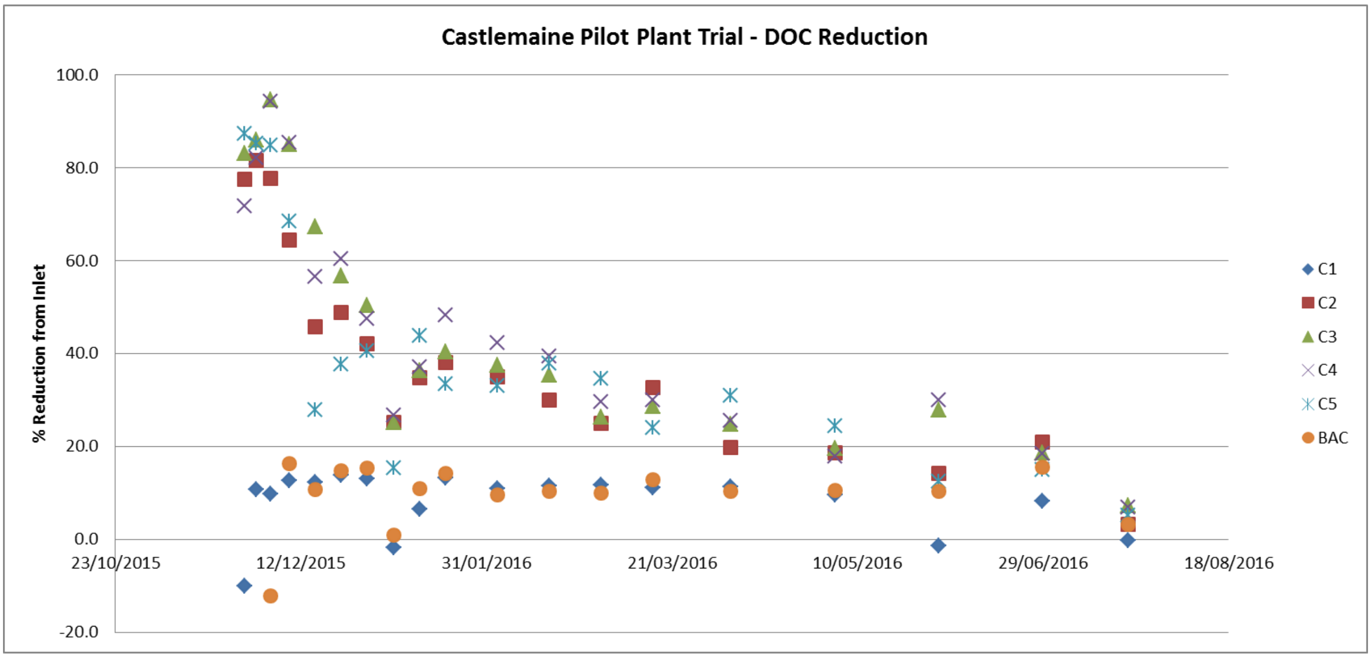

Figure 1: DOC Reduction

Sample	UV254 (Abs/cm)		Colour (CPU)		DOC (mg/L)		BDOC (mg/L)	
	Av	% Redn	Av	% Redn	Av	% Redn	Av	% Redn
C1	0.043	7	1.5	-41	3.9	8	0.8	32
C2	0.025	45	0.6	49	2.5	40	0.6	47
C3	0.021	53	0.4	65	2.2	47	0.5	51
C4	0.022	53	0.3	69	2.2	47	0.5	52
C5	0.034	56	0.6	79	2.5	41	0.4	38
BAC	0.040	13	0.8	25	3.7	12	0.8	30
Inlet/ O3	0.046	41	1.1	59	4.2	1	1.1	-65
CMF	0.078		2.6		4.3		0.7	

Table 2: Percent Organics Reduction (All Data)

In ozonated feed water, Acticarb GS1300 had consistently better organics reduction -

	GS1300 (columns 3/4)	GA1000N (column 2)	GS1300 <u>no ozone</u> (column 5)
average DOC reduction	:47%	40%	41%
average BDOC reduction	:52%	47%	38%
average UV254 reduction	:53%	45%	56%
average colour reduction	:67%	49%	79%

Ozonation significantly reduced Inlet water colour and UV254 (59 and 41% respectively). Ozonation increased the BDOC concentration of the feed water by 65%.

Column 5 showed slightly lower BDOC concentration (average 0.4 mg BDOC/L) than the columns fed with ozonated water.

After the initial adsorptive period the average DOC reduction was between 25 and 30% for the virgin carbons and 8% for Column 1 (Table 3). As the water temperature dropped the % average DOC reduction also dropped with Columns 3/4 showing the best DOC reduction at 18%. Column 5 (non-ozonated) showed similar DOC reduction at 14%. Column 1 consistently had the poorest performance for DOC reduction and the full scale plant showed better DOC reduction, suggesting that the more well-established biological component of the filters was more successful than the younger pilot scale columns. This might be an indicator that they need a longer EBCT or less frequent backwashing as water temp drops.

Table 4 shows that the BDOC concentrations in the effluent leaving the ozonated columns were very similar (0.5-0.6mg/L) even when the water temperature dropped.

Percent DOC Reduction				
	All Data	**Steady State**	**Steady State >15°C**	**Steady State <15°C**
n	*19*	*11*	*7*	*4*
Column 1	8	8	11	4
Column 2	40	25	31	14
Column 3	47	28	33	18
Column 4	47	30	36	18
Column 5	41	27	34	14
BAC	12	11	11	10

Table 3: Percent DOC Reduction

	Steady State		**Steady State (<15°C)**	
	Av BDOC (mg/L)	**% Reduction**	**Av BDOC (mg/L)**	**% Reduction**
Inlet/ O3	1.0		0.8	
C1	0.6	34	0.6	42
C2	0.6	40	0.5	45
C3	0.6	39	0.6	42
C4	0.6	42	0.5	47
BAC	0.7	30	0.6	42
Inlet/ CMF	0.5		0.3	
C5	0.4	23	0.3	<1

Table 4: Percent BDOC Reduction

3.3 MINERAL CONTENT

Table 1 shows that the aluminium, iron and manganese levels throughout the trial were relatively low. There was an increase in manganese concentration in the feed water in May and June and the best performing BAC filter was the full scale plant, closely followed by Column 5 (the non-ozonated column) and Column 1 (the old media) (Table 5). The better performance of the older more biologically adapted carbon suggests that the mechanism for manganese reduction is biological rather than adsorptive.

	Column 1	Column 2	Column 3	Column 4	Column 5	BAC	Inlet/ O3	CMF
4/05/2016	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.025	0.015
1/06/2016	0.008	0.029	0.010	0.019	0.008	0.002	0.051	0.043
29/06/2016	0.003	0.017	0.009	0.021	<0.001	<0.001	0.020	0.012

Table 5: Soluble Manganese Concentrations During Winter

Calcium levels in the feed water and pilot column effluents showed slightly higher concentrations of calcium in the water after BAC filtration. This suggests that any accumulation of calcium on the carbon media is due to biological activity rather than adsorption, e as the bacteria consume oxygen and release CO2, the calcium is being deposited as calcium salts.

3.4 PHYSICAL FILTRATION

In addition to being an adsorptive media, activated carbon is a physical filtration media. Table 6 summarises the operational conditions throughout the trial and shows that the carbon columns have good filtered water quality.

Sample	pH			Turbidity (NTU)		
	Average	Min	Max	Average	Min	Max
C1	6.7	6.5	7.1	0.2	0.1	0.3
C2	6.7	6.6	7.1	0.2	0.1	0.4
C3	6.8	6.6	7.1	0.2	0.1	0.4
C4	6.8	6.6	7.1	0.2	0.1	0.6
C5	6.8	6.3	7.1	0.2	0.1	0.5
BAC	6.9	6.8	7.1	0.2	0.1	0.2
Inlet/ O3	7.0	6.7	7.1	0.2	0.1	0.5
CMF	6.9	6.7	7.1	0.2	0.1	0.2

Table 6: pH and Turbidity Levels

3.5 BIOLOGICAL INDICATORS

Dissolved oxygen, plate counts and ATP concentrations of the column effluents were used as indicators of biological stability. Figure 2 shows that initially there were high levels of colony forming units in the column effluents as the biological populations stabilised. Towards the end of the experiment there were significantly lower plate counts in the pilot columns filter effluent suggesting the populations were more stable.

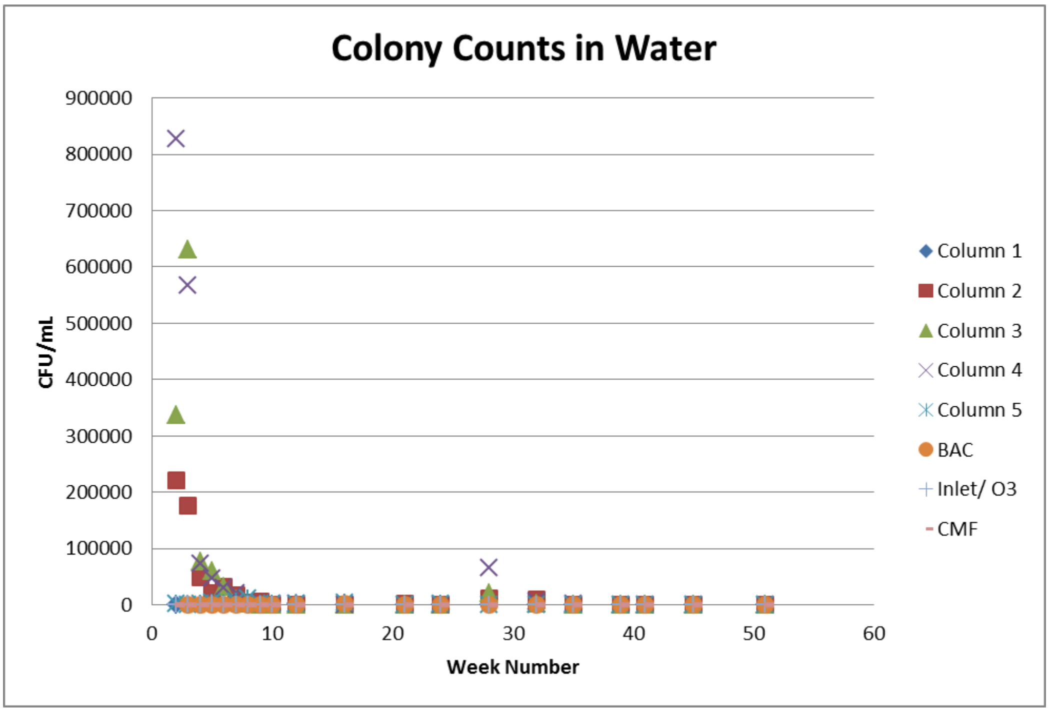

Figure 2: Bacterial Plate Counts in Column Effluent

Dissolved oxygen levels in the column effluents (Table 7) showed a consistent decrease from the feed water (both in the ozonated feed water and non-ozonated feed water). Column 1 had slightly higher DO reductions (average 2.2ppm reduction across the column) than the newer carbons (Columns 2, 3 and 4 had an average reduction of 1.8ppm)

Sample	Average DO (ppm)
C1	7.4
C2	7.9
C3	7.8
C4	7.7
C5	8.0
BAC	7.8
Inlet/ O3	9.6
CMF	8.5

Table 7: Dissolved Oxygen Levels

In addition to analysis of the water, samples of the media were analysed for plate counts, ATP, SEM and DNA profiling. Each of these methods contributes different things to the biological profile. Plate counts and ATP provide a quantitative measure with no consideration of size of each organism. DNA profiling provides a quantitative measure of the types of organisms present however again organisms in abundance can potentially mask the presence of species in lower numbers. SEM is a snap shot of the biological ecosystem however this may not be representative of the entire population.

Table 8 shows that initially there were high plate counts on the media. This correlates strongly with the high plate counts of the water during this time suggesting that the biological density was not yet stable (easily extracted from the carbon media). Column 5 looked to be impacted more significantly during the cooler months with lower plate counts on the media compared to the columns with ozonated feed water. The low BDOC reduction through Column 5 during winter could be attributed to the low plate counts.

	Media Colony Counts (CFU/mL)				
	Column 1	Column 2	Column 3	Column 4	Column 5
9/12/2015	14,000	1,010,000	1,933,333	1,530,000	63,000
4/05/2016	18,667	20,500	68,000	78,500	7,500
8/09/2016	47,333	87,333	66,000	103,500	2,500
30/11/2016	114,667	170,500	78,333	132,000	89,000

Table 8: Media Colony Counts

Table 9 shows ATP measurements of the media. The September data shows lower ATP concentration in the media throughout all the columns most likely due to the cooler water temperatures. In warmer weather the ATP concentration on the GS1300 (Columns 3 and 4) was significantly higher (up to 46%) than the GA1000N however plate count data showed higher densities only in the colder water. The ATP measurement does not require an extraction procedure (like plate counts) and instead measures the total concentration of ATP present on the media. Higher plate counts may suggest bacteria are not as tightly bound to the media and more easily extracted and plated.

	Media tATP (x10^5 pg/g BAC)				
	C1	C2	C3	C4	C5
4/05/2016	3.28	1.52	1.59	1.45	2.66
8/09/2016	1.38	1.05	1.22	1.09	1.67
30/11/2016	2.72	1.67	3.12	2.79	2.36

Table 9: Media ATP Measurements

There is significant variation between ATP measurements and media colony counts, particularly during establishment of biomass and with seasonal changes in influent quality, water temperature and biological metabolic processes. However, regular sampling of full scale BAC filters at varying depths will enable a comprehensive database of biological activity within filter media to be built for a specific treatment plant. In time, such a database will allow more rigorous data analysis, with the ultimate outcome being to use an easily measured parameter such as ATP to provide a rapid indication of the health of the BAC biomass and an indication of expected performance in terms of removal of BDOC and other contaminants. Ultimately the water quality is the most important operational consideration.

DNA profiling (conducted by the AWQC: Figures 3 and 4) of the May and November 2016 collected media samples showed greater biological diversity on the non-ozonated column 5 media compared to the columns with ozonated feed water. The Acticarb GS1300 also showed greater biological diversity than Column 2 which contained Acticarb GA1000N.

The DNA profiling showed proteobacteria as the predominant species in all the columns and many of the most common heterotrophs and manganese oxidising species are in this category.

Bacteriodetes appeared more abundant in all samples in November. The AWQC describes these as oligotrophs, adapted to survive in environments that offer very low levels of nutrients and present in freshwater. These species stick to surfaces with the aid of a holdfast, producing a biofilm which was evident in SEM photographs.

SEM photographs showed Column 5 did have a noticeably different biofilm distribution. There were a lot more and a greater assortment of rod-shaped bacteria that could be seen and gallionella were present for the first time.

May 2016 November 2016

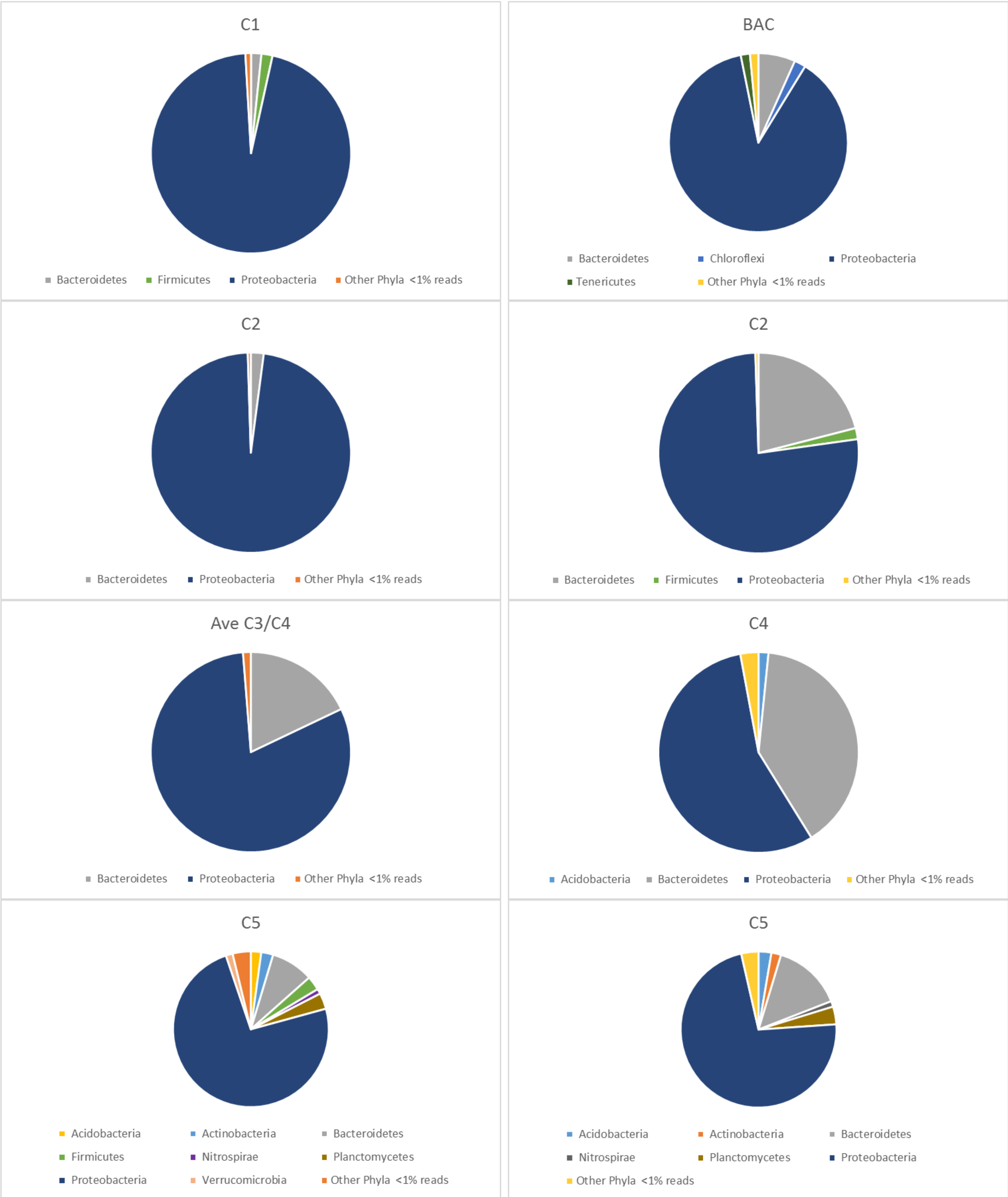

Figure 3: DNA Profiles - Phylum

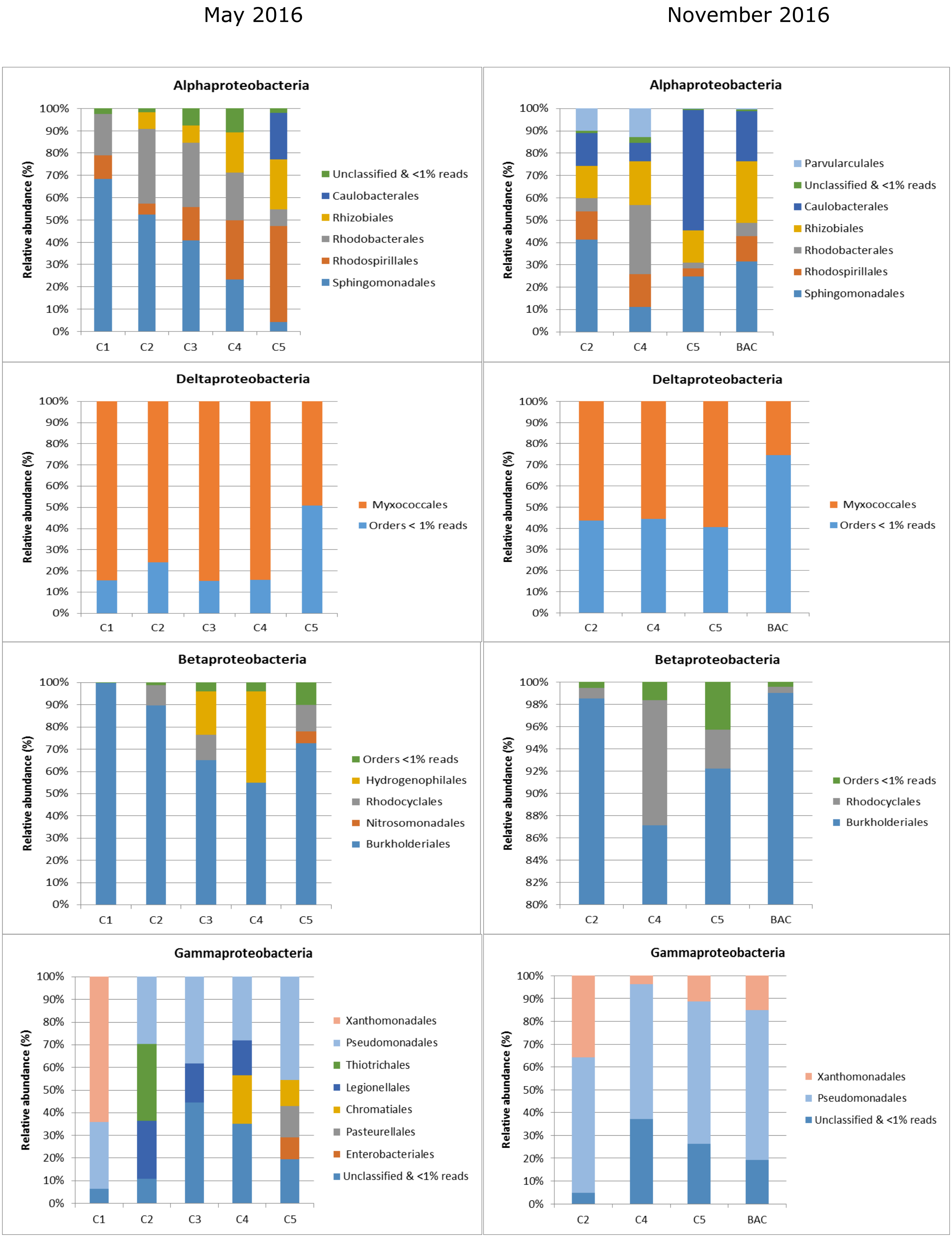

Figure 4: DNA Profiles – Proteobacteria Orders

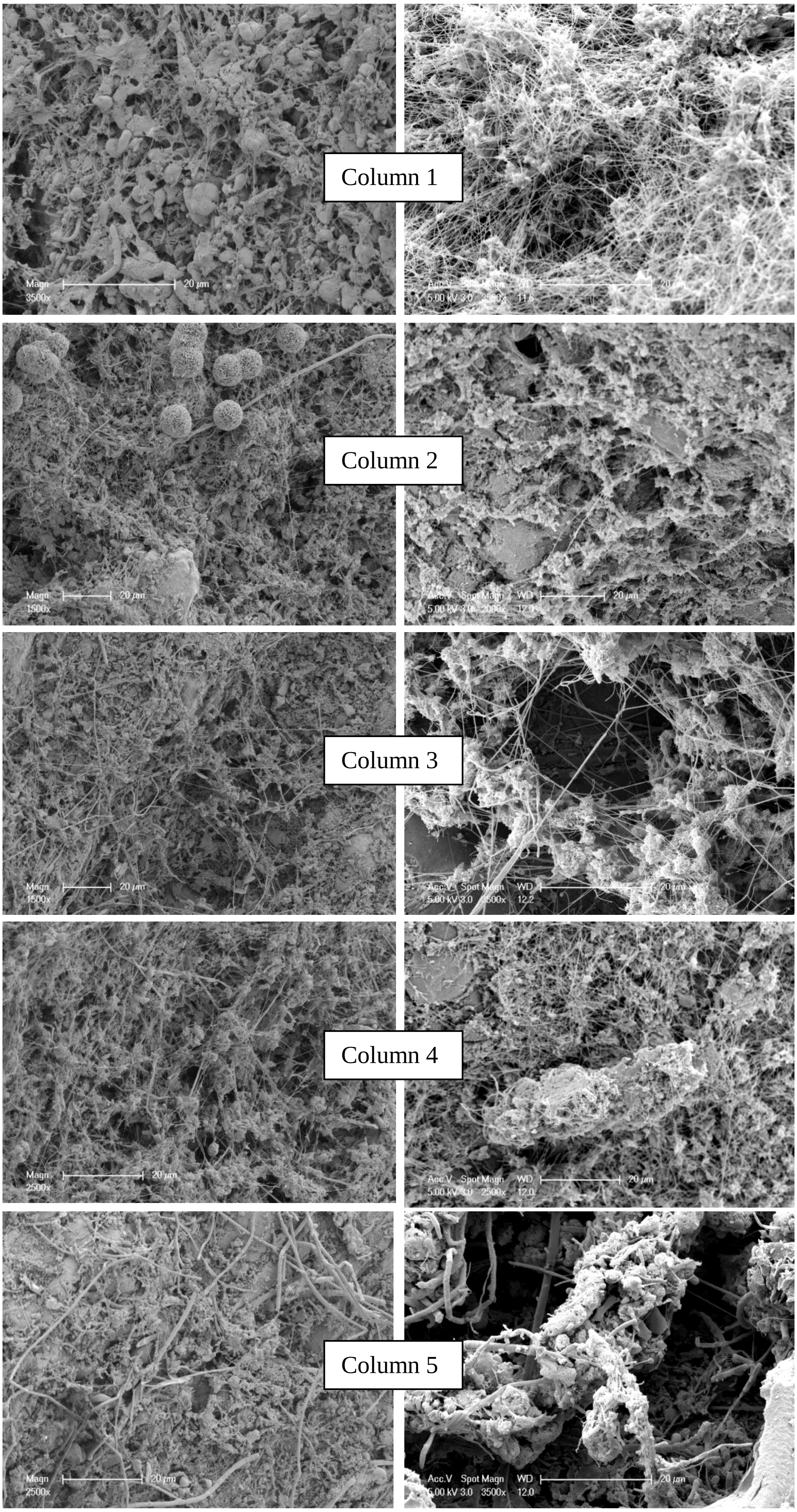

Figure 5: SEM Photographs (May on the Left, November on the Right)

3.6 ACTIVATED CARBON ANALYSIS

Table 10 shows analysis of the carbon media after the pilot plant project and compared it to the original virgin carbon. After 12 months of operation the adsorptive capacity (iodine number) of the carbon dropped and although the Acticarb GS1300 had a higher iodine number initially, the iodine number at the end of the project was very similar to the Acticarb GA1000N. Both GS1300 carbon samples, with the non-ozonated and ozonated feed waters, had similar iodine numbers and mineral levels. This suggests that the number of adsorptive sites available for biological regeneration were similar for both carbons and during both operating conditions.

Levels of calcium, manganese, phosphorus and sulphur all increased during the pilot plant operation however calcium and manganese levels were still significantly less than the "in-use" carbons in Column 1 and the full scale BAC filters.

Sample	Iodine Number	Total Ash Content (%)	Acid Soluble Ash Content (%)	Acid Soluble Ash Composition (mg/ g AC)						Volatile Content (%)
				Al	Ca	Fe	Mn	P	S	
GA1000N (virgin)	921	5.6	4.6	5.4	2.7	4.9	0.1	<0.5	2.7	
GS1300 (virgin)	1278	13.2	8.7	39.0	8.2	36.5	0.9	1.8	5.5	
BAC	302	18.1	11.8	31.3	101.7	8.9	26.3	1.4	16.8	28.6
Column 1	441	11.4	8.6	34.6	76.9	8.7	16.9	0.7	17.8	27.7
Column 2	681	4.8	1.9	4.8	10.0	4.4	0.9	<0.5	7.7	12.8
Column 3	671	17.9	5.1	21.4	16.6	25.9	2.6	1.0	12.4	14.7
Column 4	738	12.9	5.6	26.4	18.6	27.0	3.0	1.2	13.2	14.3
Column 5	719	10.7	6.2	24.9	24.4	25.5	2.4	0.8	16.0	18.6

Table 10: Activated Carbon Analysis

4 CONCLUSIONS

Pre-ozonation and carbon type did influence the treated water quality. Although pre-ozonation provides significant reduction in colour and UV254, it is predominantly the BAC filtration process that reduces the DOC of the treated water. Initially the Acticarb GS1300 showed higher adsorptive capacity for DOC after ozonation than the Acticarb GA1000N. During steady state this trend continues with the GS1300 (columns 3 and 4) having slightly higher organics reduction than GA1000N (Column 2). Without the presence of ozone the BDOC concentration of the feed water was significantly less and consequently the BDOC of the BAC filtered water of Column 5 was slightly less than the ozonated columns. Temperature of the feed water also influenced the performance of the non-ozonated column to remove BDOC more-so than the ozonated columns. This decrease in BDOC reduction during winter in Column 5 correlated with lower biological indicators (plate counts and ATP) on the media itself.

DNA profiling showed greater biological diversity on the non-ozonated Column 5 media compared to the columns with ozonated feed water. This was also observed in the SEM photographs. The Acticarb GS1300 (Columns 3 and 4) also showed greater biological diversity than Column 2 which contained Acticarb GA1000N.

The DNA profiling showed proteobacteria as the predominant species in all the columns and many of the most common heterotrophs and manganese oxidising species are in this category.

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